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Use of Industrial Hygiene Samplers for Soil-Gas Measurement

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THE USE OF INDUSTRIAL HYGIENE SAMPLERS FOR SOIL-GAS MEASUREMENT

by

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16. ABSTRACT

This report describes a field evaluation of a passive-sampling technique for soil-gas surveying. The system uses a sampler, consisting of an industrial hygiene organic vapor monitor inside a metal sampling manifold, buried at a depth of approximately 0.3 meters (1 foot). Samplers are analyzed off site by NIOSH Method P&CAM 127.

For passive sampling in general and this technique in particular, an absorbent sampler is buried at a shallow depth and allowed to collect VOCs from the soil atmosphere. After a set time (8 hours to several weeks), the sampler is retrieved, sealed immediately, and transported to a laboratory for analysis. Analysis results indicate the identity and concentration of VOCs collected by the sampler. The main advantage of passive sampling lies in the simplicity of field operations i.e. field support (supplies, personnel, and equipment) is much less costly than for grab sampling, and equipment problems are virtually non-existent. The disadvantages associated with passive sampling are that results are not available for days to weeks and that deep sampling is difficult without more elaborate equipment.

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ABSTRACT

The Lockheed Passive Sampling System (LPSS) for soil-gas measurement was field-tested at the Pittman Lateral near Henderson, Nevada. The system uses a sampler, consisting of an industrial hygiene organic vapor monitor inside a metal sampling manifold, buried at a depth of approximately 0.3 meters (1 foot). Samplers are analyzed off site by NIOSH Method P&CAM 127.

At the Pittman Lateral, unconfined ground water occurs at 1.5 to 4.3 meters (5 to 14 feet) beneath the ground surface. Two distinct ground-water volatile organic contaminant plumes exist at the site: one is primarily chloroform, and the other, benzene and chlorobenzene. Both plumes have been delineated by repeated sampling and analysis of ground water from monitoring wells located at 64-meter (200-foot) intervals along a line perpendicular to the direction of ground-water flow. In a previous study funded by the U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, Nevada (EMSL-LV), a grab-sample/on-site analysis technique and a different passive-sample/remote analysis method were field-tested at the same site.

The LPSS technique successfully delineated a chloroform soil-gas plume above ground water contaminated with chloroform at concentrations as high as 800 μg per liter. The chloroform soil-gas concentrations at a depth of 0.3 meters (1 foot) measured by LPSS correlate strongly with soil-gas concentrations at 1.3 meters (4 feet) measured in the earlier grab-sample/on-site analysis study. The results of the LPSS method also correlate well with ground-water chloroform concentrations. The variability among results separated by short distances (*ca* 1 meter) was less than that for grab sampling with on-site analysis and was between 12 and 22 percent relative standard deviation. The variability among 10 samplers over a 8.3-meter (27-foot) distance parallel to the direction of ground-water flow was 12 percent relative standard deviation. The precision of the LPSS results was used to estimate an empirical relationship for the spatial resolution for the technique at this site. This spatial resolution was between 3.1 and 6.2 meters (10 and 100 feet), depending on the concentration of chloroform in the soil gas. The efficiency of the sampler is seen to vary with chloroform concentration, suggesting a possible concentration-dependent humidity effect. LPSS measurements were also made at four locations in a 1-meter (3-foot) square pattern above ground water containing approximately 5000 μg per liter benzene and 4000 μg per liter chlorobenzene. Although the samplers were buried for three months, no detectable amounts of benzene or chlorobenzene were measured upon analysis. Aldehydes, esters, and ethylene dibromide were detected on the samplers. These results agree with results from the earlier study and are consistent with subsurface oxidation eliminating benzene and chlorobenzene from the vadose zone.

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INTRODUCTION

OBJECTIVES AND GOALS

This report describes a field evaluation of a passive-sampling technique for soil-gas surveying. The field evaluation was performed at a site where other soil-gas measurement methods have been evaluated (1). The objectives of the evaluation were: to determine the degree of correlation of results with those from a previous grab-sample survey at the site, to assess the correlation of results with ground-water volatile organic compound (VOC) concentrations, to evaluate the precision of results from closely spaced samples as a function of VOC concentration, to estimate the spatial resolution of the method, and to test the sampler/manifold assembly for its efficiency in trapping VOCs in the field.

BACKGROUND

General

Sampling and analysis for evaluation of contamination of soil and ground water by organic compounds is traditionally performed by drilling boreholes and collecting and analyzing soil cores and ground-water samples. Because of the high cost and slow turnaround time of analyses, workers in the area of site-characterization have turned to alternative rapid, inexpensive preliminary field-reconnaissance techniques for guidance in selecting the most appropriate locations for ground-water sampling. For highly conductive dissolved ground-water contaminants (electrolytes) such as salts and strong acids or bases, measurement of the conductivity of ground water by surface geophysical techniques has been successful (2). However, for organic contaminants such techniques are not applicable since these compounds rarely alter the electrical properties of ground water. For organic compounds which are volatile, soil-gas measurement has emerged as a cost-effective reconnaissance technique for preliminary site characterizations (1,3,4).

Organic compounds are a major threat to aquifers because of their potential long residence times (5). Due to their high activity, VOCs are more mobile than other compounds. Table 1 shows a list of the 25 most frequently identified substances regulated under the Comprehensive Environmental Response Compensation and Liability Act, (CERCLA or Superfund); of these, 15 are VOCs amenable to soil-gas surveying. In addition, studies at the U.S. EPA Environmental Monitoring Laboratory in Las Vegas, Nevada (EMSL-LV) have shown that VOCs are typically the first detected when ground water is being contaminated by leaching from a hazardous-waste disposal site (6). Major components of gasoline and jet fuels are also VOCs, so that soil-gas measurement is applicable to mapping the areal extent of contamination from such mixtures (7) and can be the basis of leak-detection systems for underground storage tanks (8). The behavior of VOCs in the subsurface and the principles behind soil-gas surveying are discussed below.

Volatile Organic Compounds in the Subsurface

When VOCs are present in the subsurface, either in an organic liquid phase or dissolved in ground water, several processes, under both thermodynamic and kinetic control, can take place In the saturated zone VOCs can undergo sorption to organic matter in the soil, liquid diffusion,

TABLE 1. MOST FREQUENTLY IDENTIFIED SUBSTANCES AT 546 SUPERFUND SITES[a]

Rank	Substance	Henry's Law Constant[c]	Percent of Sites
1	Trichloroethylene*	0.38	33
2	Lead and compounds[b]	NA	30
3	Toluene	0.23	28
4	Benzene	0.24	26
5	Polychlorinated biphenyls (PCBs)	~0	22
6	Chloroform*	0.15	20
7	Tetrachloroethylene*	0.59	16
8	Phenol	~0	15
9	Arsenic and compounds[b]	NA	15
10	Cadmium and compounds[b]	NA	15
11	Chromium and compounds[b]	NA	15
12	1,1,1-Trichloroethane*	0.67	14
13	Zinc and compounds[b]	NA	14
14	Ethylbenzene*	0.28	13
15	Xylene*	0.20	13
16	Methylene chloride*	0.08	12
17	*trans*-1,2-Dichloroethylene	0.33	11
18	Mercury and compounds[b]	NA	10
19	Copper and compounds[b]	NA	9
20	Cyanides (soluble salts)[b]	NA	8
21	Vinyl chloride*	47 (10°C)	8
22	1,2-Dichloroethane*	0.044	8
23	Chlorobenzene*	0.14	8
24	1,1-Dichloroethane*	0.23	8
25	Carbon tetrachloride*	1.0	7

*Compounds amenable to detection by soil-gas analysis.
[a] Adapted from Reference 1.
[b] This class of compounds is almost invariably non-volatile.
[c] Henry's Law constant is the equilibrium gas concentration (μg/L) of a volatile compound divided by its concentration in water (μg/L) at 25°C.
NA Not available.

vertical and horizontal mixing due to dispersion, biotransformations, and chemical reactions (5). In the vadose (unsaturated) zone the vapors from these VOCs can undergo gas-phase diffusion, vapor/sorption equilibria, vapor/solution equilibria, biotransformations, and chemical reactions. In the intermediate zone (capillary fringe) the potential can exist for any of the above processes to occur. By definition, the capillary fringe is fully saturated. The water there is held by capillary forces or soil suction, and so is under less than atmospheric pressure. In actuality, heterogeneity in the size and shape of vadose zone materials can result in the presence of adjacent air-filled and water-filled channels in the capillary fringe.

Although there are many processes that can affect VOCs in the subsurface, the list of processes that are important where soil-gas surveying is applicable is extremely limited. In order to detect VOCs in soil gases above contamination, the rate of introduction of VOCs into the soil atmosphere must be sufficient to maintain a measureable VOC concentration there. That situation will occur only when the rate-limiting step in vertical transport of VOCs from the contamination (source) to the atmosphere (sink) is diffusion through the vadose zone. Under such conditions, the VOC vapor concentration above the capillary fringe/vadose zone interface will be at a concentration controlled by a dynamic vapor/solution equilibrium, while VOC concentrations in soil gases between there and the soil surface will be determined by the rate of diffusion of the gases through the soil (9). Figure 1 depicts idealized VOC transport from ground water to the atmosphere.

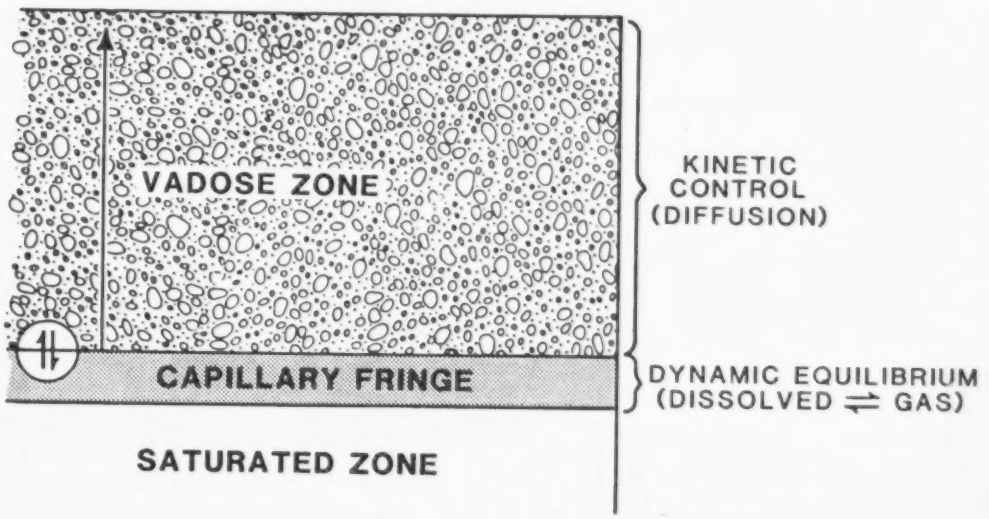


FIGURE 1. VOC TRANSPORT FROM THE WATER TABLE TO THE ATMOSPHERE

Fick's Laws describe the process of diffusion (10); these equations have been modified extensively to describe diffusive flow through porous media (11,12). Fick's Law for VOC diffusion in air through a unit area, as corrected for available air-filled pore space, is:

$$\text{mass flow} = -D_a \cdot P \cdot (C_s - C_a)/Z \qquad (1)$$

where D_a is the gas-phase diffusion coefficient, P is the air-filled porosity, C_s is the gas-phase VOC concentration at the capillary fringe, C_a is the concentration at the soil surface, and Z is the depth from the surface to the capillary fringe. Millington and Quirk have

derived an expression based on Fick's Law, for diffusion of gases through soils, that is modified for the tortuosity (non-linearity) of diffusion paths through porous media (13). In that description of diffusion in soils the gas-phase diffusion coefficient, D_a, of the diffusing compound is modified for tortuosity by multiplying it by P_a, the air-filled porosity of the soil, raised to the 4/3 power. **Equation 1**, when modified for tortuosity (13) becomes:

$$\text{mass flow} = -D_a \cdot P_a^{1/3} \cdot P_a \cdot (C_s - C_a)/Z \qquad (2)$$

for dry soil, where $P_a^{1/3}$ is the term incorporated to describe the tortuosity of porous media. Other modifications of Fick's Law to account for tortuosity have also been formulated (12). Moist soil requires the multiplication of the right-hand side of **Equation 2** by P_a^2/P_c^2, where P_t is the total porosity of the soil.

Equation 2 predicts a linear concentration gradient with depth under homogeneous conditions. A strong linear depth dependence of the VOC concentration in soil gas has been observed at the site of this study (1) and in other field (3) and laboratory (9, 14) studies. Non-kinetic factors, such as equilibrium sorption on soil, are not relevant to discussion of the kinetically controlled VOC concentrations in the vadose zone that exist when soil-gas surveying is applicable.

The VOC concentration gradient between the atmosphere and the soil gas in contact with the capillary fringe is the driving force for the diffusional vertical transport of VOCs. The concentration of VOC in the gas phase in contact with the capillary fringe is dictated by a dynamic equilibrium between the dissolved and the gas-phase VOC. The physical-chemical expression which describes this equilibrium is Henry's Law (15).

The Henry's Law constant of a VOC can be obtained by dividing the vapor pressure of the pure VOC by its solubility in distilled water. Table 1 lists the Henry's Law constants for several VOCs of interest; however, these values should be used only for guidance as to the relative suitability of the VOC for detection by soil-gas measurement. This is because the ambient pressure, organic content of the soil, temperature, and ionic strength of the water encountered in the field can modify the situation from the conditions used to determine the tabulated values.

So, VOC concentrations in soil gases in the vadose zone are determined by equilibrium considerations at the capillary fringe and kinetic factors in the vadose zone. Under circumstances controlled by equilibrium factors, kinetic considerations such as vaporization rates are not of concern. In situations where the rate of processes control the situation (kinetic control), equilibrium considerations are important only to indicate the direction of change. It is important to not confuse these concepts in order to effectively plan and interpret soil-gas surveys.

Passive and Grab Sampling Techniques in Soil-gas Sampling

Soil-gas measurement was originally developed in the 1920's for petroleum exploration (16). Recently, the technology has been used for delineation of the extent of contamination by VOCs (4,17). Soil gases are typically sampled by one of two approaches: grab sampling and passive sampling.

In grab sampling, a hollow pipe is driven into the ground to a prescribed depth and soil gases are withdrawn through it. Samples are then analyzed by gas chromatography at or near the sampling location. This method offers the benefit of immediate results, a feature which is attractive because it allows the sampling plan to be modified as the survey progresses. In addition, preliminary measurements can be performed to allow investigators to optimize certain survey parameters, such as sampling depth. An advantage of this approach is that in addition to on-site screening of soil gas, analysis of soil and ground-water samples can be performed. The

drawback of this approach is that it is expensive, in that it requires sophisticated sampling and analytical equipment, a specialist to operate and maintain it, and associated support systems (*e.g.*, generators, compressed gases).

In passive sampling, an absorbent sampler is buried at a shallow depth and allowed to collect VOCs from the soil atmosphere. After a set time (8 hours to several weeks), the sampler is retrieved, sealed immediately, and transported to a laboratory for analysis. Analysis results indicate the identity and concentration of VOCs collected by the sampler. The main advantage of passive sampling lies in the simplicity of field operations; field support (supplies, personnel, and equipment) is much less costly than for grab sampling, and equipment problems are virtually non-existent. The disadvantages associated with passive sampling are that results are not available for days to weeks and that deep sampling is difficult without more elaborate equipment.

Soil-gas surveying technologies are designed as reconnaissance tools, to be used in conjunction with ground-water quality data, not to replace it. Confirmation of the predictions of contamination from soil-gas results, based on analysis of soil cores and ground-water samples, will always be necessary. However, a preliminary soil-gas survey can help site investigators plan a more cost-effective effort.

Based on the advantages and disadvantages of the two approaches to soil-gas surveying, site investigators can choose one or the other depending on the priorities of the particular task at hand. In general, passive sampling will be preferable when there is already some knowledge of site conditions, so that sampling locations can be chosen ahead of time, and for smaller surveys (less than 40 points). Examples of situations where passive sampling would be preferable include: evaluating the possibility of VOC migration onto or away from a site, clarifying of the situation between monitoring wells or in a specific area, and for periodic (*e.g.*, monthly) monitoring of vapor wells for detection of leakage from underground storage tanks. On the other hand, grab sampling techniques are preferable where the situation is very poorly defined or the effort is exploratory and a high potential for changes in the initial sampling plan exists. Grab sampling is also useful where the availability of analytical equipment is desirable for screening soil and ground-water samples. For grab sampling to be cost-effective, the survey must be of sufficient size to justify the mobilization and operation costs associated with the use of on site analytical equipment.

A private firm has developed a passive-sampling device for oil exploration and has also used it for mapping ground-water VOC contamination (18,19). Although the sampler is said to measure the "integrated VOC flux" at sampling locations, no rigorous evaluation of it has been performed. One publication, indicating the potential of the technique for application to ground-water contamination, showed that it measured high levels of toluene, carbon tetrachloride, and dichloroethylene in the headspace above a well. However, analysis of ground-water samples from that well did not show detectable concentrations of these compounds (19). In addition, the technique failed to detect chloroform, although that compound was the major containment, as measured in the gas chromatography/mass spectrometry (GC/MS) analysis of ground-water samples in that study (19). In a study of the technique performed by EMSL-Las Vegas above chloroform-contaminated ground water, results showed no correlation with ground-water concentrations, very poor precision among results from samplers separated by 1-2 meters (3-6 feet), and high levels of blank contamination (1). Results from a grab-sampling method used simultaneously showed good correlation with ground-water concentrations and a high level of precision (1).

Because of the failure of this passive-sampling technique where a grab-sampling method had succeeded, and due to the attractive features of passive sampling, we decided to test passive soil-gas sampling using a diffusional sampler that has been validated for workplace atmospheres.

Theory of Diffusional Sampling

Sampling for airborne contaminants was originally developed using active-sampling techniques, whereby sample air is pumped through a device containing a sorbent--for VOCs, usually a glass tube filled with activated charcoal. The mass of the vapor collected is a direct function of the sampling rate of the pump, the ambient concentration, and the sampling time. For passive sampling, vapors are also collected on a sorbent, but transport is by gaseous diffusion rather than by pumping. The mass uptake of vapor is controlled by the effective sampling rate of the sampler, which is a function of the dimensions of the sampler and the diffusion coefficients of each compound collected, ambient concentrations, and sampler exposure time. OSHA has established general precision and accuracy criteria for air sampling and analysis which must be met, for results to be considered valid measurements of workplace atmospheres (29 CFR 1910). While these criteria were originally developed for "active" sampling, they also apply to passive sampling. There are several commercially available samplers marketed for industrial hygiene use that meet the OSHA criteria.

Figure 2 shows a schematic of a typical diffusional sampler. The sorbent used for higher concentrations of VOCs is charcoal. Tenax has been used in a passive sampler developed by EPA for indoor air measurements where VOC concentrations are much lower than those of concern in soil-gas or workplace atmospheres (20,21). The draft shield shown in Figure 2 is used to ensure that the sole mechanism of VOC transport from the atmosphere to the sorbent is gas-phase diffusion. With this assumption, Fick's Law can be applied to calculate the rate of VOC accumulation on the sorbent:

$$\text{Rate} = D_a\ (A/L)\ (C_a - C_o) \qquad (1)$$

where D_a is the diffusion coefficient of the VOC in air (cm^2/sec), A is the sorbent area (cm^2), L is the diffusion path length (cm), C_a is the VOC concentration outside the draft shield (ng/cm^3), and C_o is the VOC concentration at the sorbent surface (ng/cm^3). For a charcoal sorbent, C_o is assumed to be zero for most VOCs, and equation 1 becomes:

$$\text{Rate} = D_a\ (A/L)\ (C_a) \qquad (2)$$

so that the rate of VOC accumulation (ng/sec) is equal to the ambient VOC concentration multiplied by the term $D_a(A/L)$. The term $D_a(A/L)$ can be expressed in units of cm^3/sec and can be considered to be the volume (in cm^3) scrubbed free of VOCs in one second.

Although the variables A (sorbent area) and L (diffusion path length) are not influenced by the variables that affect gases (pressure and temperature), the sensitivity of the diffusion coefficient of the VOC, D_a, to these parameters must be considered. If it is relatively insensitive, concentrations of VOCs at sampling locations can be calculated directly from the amount accumulated and the term $D_a(A/L)$.

Diffusion coefficients determined empirically are available for many volatile organic compounds, or can be calculated to within 5% (22) by:

$$D_a = 4.3 \times 10^{-3}\ (M_r)^{1/2}\ (T)^{3/2}\ P^{-1}\ (V_a^{\ 1/3} + V_b^{\ 1/3})^{-2} \qquad (3)$$

where D_a = diffusion coefficient of the VOC, T = absolute temperature (K), M_r = reduced mass of air and the VOC ($M_r = (M_a + M_b)/(M_a \cdot M_b)$ M_a = molecular weight of the VOC, M_b = molecular weight of air (28.97)), P = atmospheric pressure (atm), V_a = molar volume of the VOC (cm^3/mol), and V_b = molar volume of air (20.1 cm^3/mol).

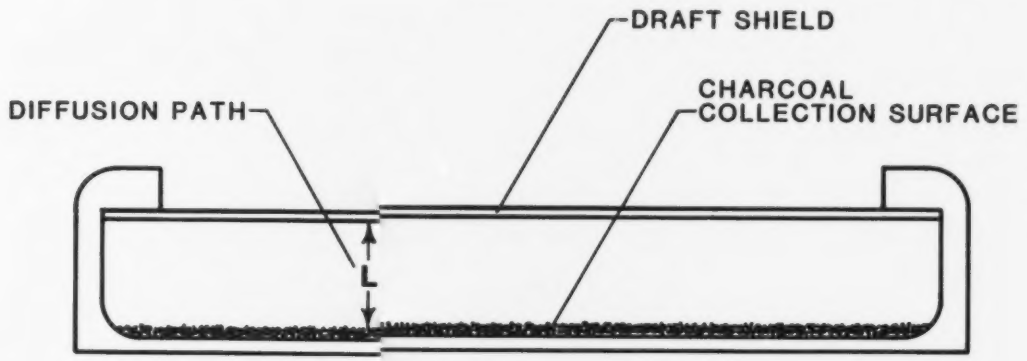


FIGURE 2. CROSS-SECTION OF A TYPICAL DIFFUSIONAL SAMPLER

By evaluation of each of the terms on the right-hand side of **Equation 3**, we can determine the effect of changes in pressure or temperature on the diffusion coefficient and thus the term D(A/L) in **Equation 2**. **Equation 3** shows that the diffusion coefficient is inversely proportional to the barometric pressure and directly proportional to the absolute temperature raised to the 3/2 power. However, as the pressure increases the decrease in the diffusion coefficient is balanced by an equal increase in the concentration so that the sampling rate is independent of pressure (23). Similarly, the increase in D_a due to an increase in temperature is partially offset by a concommitant decrease in concentration so that the net effect on the rate of VOC accumulation **Equation 2** is small (24). Even without these partial or complete obviations of the effects of changes in temperature and pressure in D_a, the result on D_a of a change in temperature from 5°C to 35°C predicted by **Equation 3** would be approximately 16 percent. However, in outdoor evaluations under a range of conditions (-15-35°C and 20-80% RH), no significant effects of T and P on sampling rate occured (20).

Based on Fick's Law, the average time required for a molecule to diffuse through the static air layer of length L in the sampler would be:

$$t = L^2/2D_a \quad \text{(seconds)} \qquad \textbf{(4)}$$

For example, for a VOC with $D_a = 0.12\ cm^2/sec$, and a diffusion path length, L, of 0.65 cm, the average time for the VOC to diffuse from the draft shield to the sorbent is 1.76 seconds. Therefore, diffusional sampling occurs rapidly even though a static air column is used.

Sampling by charcoal (or other sorbent) diffusional samplers is limited by the capacity of the sampler for various VOCs. This capacity must be determined on a compound-specific basis. In addition, studies of the use of these samplers in the atmosphere have shown that wind velocity and angle of incidence have a minimal effect on the sampling rate. Wind is not a factor in soil-gas sampling, but the very fact that the atmosphere being sampled is static could create a situation where the VOC mass transfer onto the sorbent is limited by (slow) VOC transport from the vadose zone to the draft shield of the monitor. If such a situation does occur, the VOC transport is non-steady-state and a considerably more detailed mathematical description than above is necessary (26). This description would require parameters which are not readily available for most sites.

Although VOC sorption on charcoal is considered irreversible for most compounds, there is evidence for loss of some weakly sorbed VOCs during storage between sampling and analysis (27). The performance of charcoal-sampling devices sold for industrial-hygiene applications has been studied for various compounds. Although recoveries obtained for certain compounds can vary from 100 percent depending on monitor design, they are reproducible enough for application of a correction factor (27). Such a correction is a standard practice (28).

Analysis of these monitors is performed according to NIOSH method P & CAM 127; this method involves solvent-desorption and analysis of the resulting solution by gas chromatography (29). The method has been evaluated for many VOCs of interest for soil-gas surveying and the precision and accuracy are documented (29). The method gives quality control procedures and outlines calculation methods for the analysis.

Evaluation of the application of passive sampling to VOCs in soil gases using technology that is well-described theoretically and has well-documented performance in sampling VOCs from air is a way to help characterize the soil atmosphere. If the technique which works well in air does not work or works less well in soil gases, it will indicate that different factors must be considered in sampling soil gases than in the sampling atmosphere. If the technique does work well when applied to soil-gas sampling, it presents another approach to soil-gas surveying.

CONCLUSIONS AND RECOMMENDATIONS

Results from use of the Lockheed Passive Sampling System (LPSS) for soil-gas surveying correlated well with ground-water chloroform concentrations of 10 to 1000 μg per liter above ground water that occurs at 3 to 4.5 meters (9 to 14 feet) below the ground surface. The LPSS results from measurements at a depth of 0.3 meters (1 foot) correlated very strongly with results from samples from a depth of 1.3 meters (4 feet) at the same site in an earlier grab-sample survey ($r^2 = 0.95$). The precision of measurements using the LPSS technique is superior to that obtained in an earlier grab-sample soil-gas survey at the site. Studies of the sampler efficiency indicate that at low concentrations of chloroform in the soil gas, sorption efficiency may be impaired more by the effects of humidity than at higher concentrations. An empirical statistical calculation based on the observed precision of the measurements as a function of concentration indicated that the distance between statistically signicantly different measurements at that site ranged from approximately 3 meters (10 feet) to 33 meters (100 feet), with better spatial resolution at lower concentrations.

Limited LPSS measurements above a benzene/chlorobenzene groundwater plume agreed with an earlier study that showed negligible benzene or chlorobenzene to be present in the soil gas above this highly contaminated ground water. Specific compounds identified were consistent with the occurrence of aerobic biodegradation, as postulated in the earlier study.

The LPSS technique offers superior precision, low cost, and minimal requirements for training for field personnel in comparison to grab-sampling methods. Further studies, encompassing different hydrogeologic conditions and other volatile organic compounds, are recommended. All further studies of the LPSS technique should include, for each study site, comparison of results to ground truth, closely spaced samplers to estimate overall precision, and sampling at several depths. In addition, further study of the situation in the vadose zone above the benzene and chlorobenzene contaminant plume at the Pittman site is recommended. Tests of microorganisms in the soil there for acclimation to and metabolism of these compounds should be performed. In addition, vadose-zone carbon dioxide and oxygen concentrations should be measured.

EXPERIMENTAL

SITE DESCRIPTION

Field tests were conducted at the Pittman Lateral, a site having known ground-water VOC contamination. The Pittman Lateral is a right-of-way of a major water conduit serving Las Vegas, Nevada. It is in undeveloped desert about 11 miles (18 km) southeast of Las Vegas. This site has been used since 1982 by EMSL-Las Vegas to test both surface geophysical (2) and soil-gas (1) survey methods.

At the Pittman Lateral, monitoring wells have been installed at 64-meter (200-foot) intervals along a line perpendicular to the northward direction of ground-water flow. On several occasions over the past five years, ground-water samples have been collected from these wells and analyzed for inorganic and organic contaminants. Analysis by gas chromatography/mass spectrometry of ground-water samples indicates that two distinct plumes of organic and inorganic contaminants exist at the Pittman Lateral. One plume has trichloromethane (chloroform) as its primary VOC component, while the other plume has benzene and chlorobenzene as the major VOC contaminants. Figure 3 shows the subsurface at the Pittman Lateral and the location of monitoring wells there. Table 2 lists the VOC concentrations measured in ground-water samples from monitoring wells at the site.

The hydrogeology at the Pittman Lateral is relatively simple. A clay aquiclude underlies an unconfined aquifer composed of moderately well-sorted, unconsolidated gravel alluvial deposits with discontinuous caliche cement horizons which vary in thickness from 5 to 25 meters (15 to 80 feet) (30). The ground surface, water table, and aquiclude all dip gently to the north, where the aquifer daylights at the Las Vegas Wash. Along the Pittman Lateral, unconfined ground water occurs at 1.5 to 4.3 meters (5 to 14 feet) below ground surface.

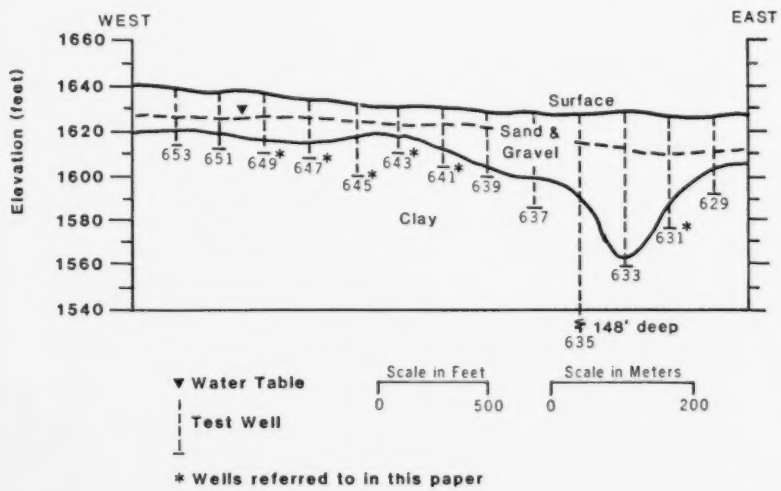


FIGURE 3. SUBSURFACE AT THE PITTMAN LATERAL

TABLE 2. CONCENTRATIONS OF CHLOROFORM BENZENE AND CHLOROBENZENE (μg/L) IN GROUND-WATER SAMPLES COLLECTED FROM WELLS ALONG THE PITTMAN LATERAL[a]

Chloroform Concentrations (μg/L)
Well Number

Date	617	619	621	623	625	627	629	631	633
3/83	d	<10	28	500	430	181	11	<10	d
11/84	s	s	s	s	850	s	s	s	s
4/85	s	s	s	570	1000	175	s	s	s
8/85	s	s	s	541	732	s	s	s	s

Benzene Concentrations (μg/L)
Well Number

Date	633	635	637	639	641	643	645	647	649	651	653
3/83	<10	340	3800	4700	3200	3400	3100	3500	1300	37	<10
11/84	s	<10	s	s	s	s	s	s	s	s	s
4/85	s	<10	s	s	5900	s	n	s	n	s	n
8/85	s	s	s	s	2548	s	3820	s	s	s	<10

Chlorobenzene Concentrations (μg/L)
Well Number

Date	633	635	637	639	641	643	645	647	649	651	653
3/83	<10	520	4000	5100	3100	2400	4700	3600	2400	800	21
11/84	s	<10	s	s	s	s	s	s	s	s	s
4/85	s	<10	s	1300	7100	s	n	s	n	s	n
8/85	s	s	s	s	4521	s	5060	s	s	s	60

a Samples analyzed by EPA Method 624 (GC/MS); detection limit = 5μg/L.
d = Not detected.
s = Not sampled.
n = Not analyzed (holding time exceeded).

The soil in the vadose zone at the site is a Caliza very-gravelly sandy loam from a sandy-skeletal, mixed, thermic family of the typic Calciorthid(31). The clay content is 2 to 8 percent decreasing with depth and the permeability is moderately high, at 5 to 15 cm per hour at depths of 0 to 40 cm and 15 to 50 cm per hour at depths of 40 to 150 cm (29). The average rainfall in the area is 10 cm with occasional periods of flooding during rainstorms. The shrink-swell potential of the soil is low (31), so that the permeability remains fairly constant when the soil is wetted. The soil is characterized by a pH of 7.9 to 8.4 and the salinity is low, with the electrical conductivity below 2 μmhos per cm(31). The organic content of the soil is extremely low.

APPARATUS AND PROCEDURES

Apparatus

The Lockheed Passive Sampling System (LPSS) is comprised of an activated carbon organic vapor monitor (No. 3500, 3M, St. Paul, Minnesota) suspended in a sampling manifold made from a one-quart can. Figure 4 shows a diagram of the LPSS assembly.

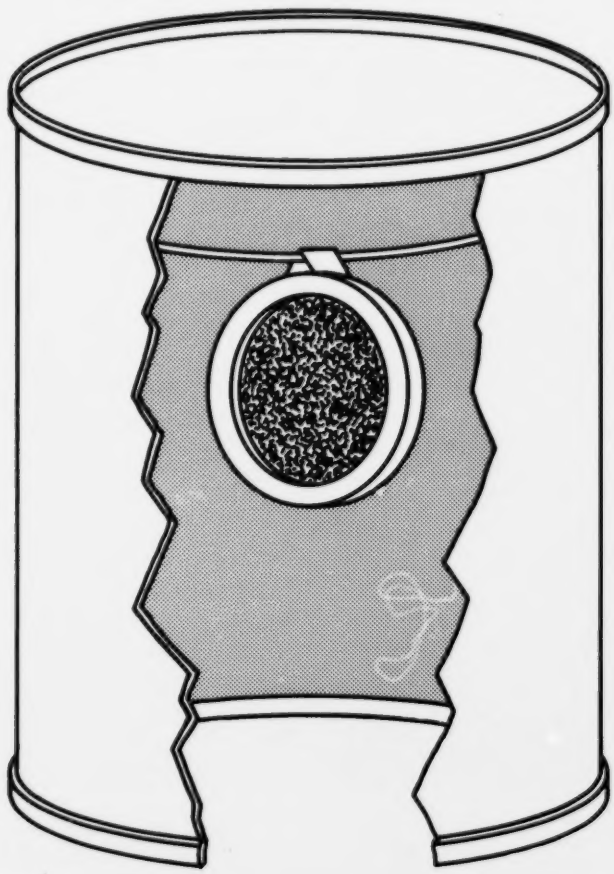


FIGURE 4. LOCKHEED PASSIVE SAMPLING SYSTEM (LPSS) SAMPLER

Field Procedures

Samplers were placed in holes 0.3 meters (1 foot) deep, the holes were backfilled, and the samplers were retrieved and sealed after a 2-week exposure period. Samplers were placed 6.4 meters (20 feet) to the north, south, east, and west of 6 adjacent groundwater monitoring wells separated by 200 feet along a line perpendicular to the northward direction of ground-water flow. At five wells, the south sampler served as the northwest corner of four samplers in a square pattern with 1-meter (3-foot) sides, while at the sixth (631), one additional sampler was placed 1-meter (3 feet) to the south of the southern sampler. A line of 10 samplers at 1-meter (3-foot) intervals was placed parallel to the direction of ground water flow, beginning at a point halfway between well 623 and 625 as a check on short-range precision along the direction of ground-water flow. A manifold with two monitors in it was placed 1-meter to the south of the sampler to the east of five wells, as a test of the sampling efficiency of the system or vertical flux. At the sixth well (631), additional samplers were placed 9.6 and 12.8 meters (30 and 40 feet) to the east of the well. Figure 5 shows the sampling locations around each well.

Analysis

Soil-gas samplers were solvent-desorbed and analyzed by gas chromatography according to the manufacturer's instructions (32). Pesticide-grade hexane (Burdick & Jackson) was used as a solvent for chloroform determinations and carbon disulfide was used for the four samplers from above the benzene/chlorobenzene plume. For chloroform, analysis was performed with a Hewlett-Packard 5710 gas chromatograph using an electron capture detector; for benzene and chlorobenzene, a flame ionization detector was used.

Calculations

From gas chromatographic analysis of a 1-μL injection of the solution containing the desorbed VOCs, the concentration of each VOC can be calculated by multiplication of the VOC peak height times the slope (ng/μL per height) of the calibration curve. Because 1500 μL of solvent was used to desorb the VOCs, the VOC concentration calculated was then multiplied by 1500 to obtain the nanograms of the VOC collected. From this value, the mean results of analysis of field blanks was subtracted. When the resulting value is divided by the sampling rate of the organic vapor monitor (in ng/ppb x hr) the average concentration (in ppb) over the exposure period results. Table 3 lists the sampling rate, recovery, and capacity of the 3M 3500 Organic Vapor Monitor for benzene, chlorobenzene, and chloroform (32).

TABLE 3. PERFORMANCE OF THE 3M 3500 ORGANIC VAPOR MONITOR

Compound	====Sampling Rate==== (cm^3/min)	(ng/ppb·hr)	Recovery(%)	Capacity (mg)
Benzene	35.5 ± 0.6[a]	6.78	102	13
Chlorobenzene	29.3 ± 0.6[a]	8.12	100	>25
Chloroform	33.5	9.78	98	7

[a] Includes 95%-confidence interval.
Source: Reference 32

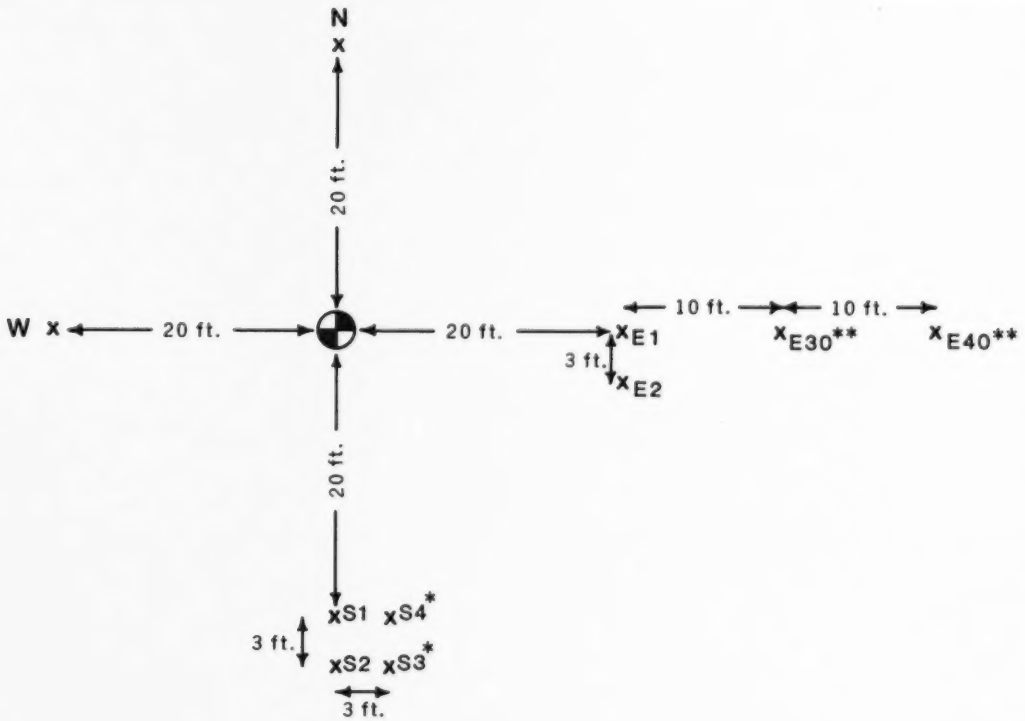


FIGURE 5. SAMPLING LOCATIONS AT THE STUDY SITE

Quality Control

Published recovery coefficients were used for chloroform desorption. Field blanks were processed and laboratory blanks were also analyzed. The detection limit was determined as three times the standard deviation of 12 non-consecutive blanks. Calibration standards were prepared by serial dilution of stock solutions prepared from neat chloroform and carbon tetrachloride (Alltech Associates, Deerfield, Illinois). Calibration was performed daily. Multiple 1-μL aliquots of desorbed solutions from each sampler were analyzed.

As a check on contributions to error and variability of results from sources other than soil gases, monitors were sealed in manifolds for four weeks and analyzed for benzene, chlorobenzene, and chloroform. Multiple 1-μL aliquots of each sample were analyzed to estimate the analysis variance. The short-range precision of results was assessed by closely spaced samplers.

EVALUATIONS

Comparison of LPSS Results with Ground-water Data

The mean LPSS results from the locations around each well were compared to the corresponding ground-water chloroform concentrations to evaluate the correlation between those two data sets. Ground-water analytical results from another EMSL-LV study (1) were used for this comparison.

Comparison of LPSS Results with Grab Sampling Data

The mean LPSS results from locations around each well were compared to grab sampling data from the earlier study.

Short Range Variability

To assess the variability of results obtained from samplers separated by short distances, multiple samplers were buried at the sampling location to the south of each well. At five of the wells (621, 623, 625, 627, 629), the location 6.4 meters (20 feet) to the south was the northeast corner of a 1-meter (3-foot) square pattern of samplers. At the other well (631), a sampler was placed 7.4 meters (23 feet) south of the well in addition to the one 6.4 meters (20 feet) south.

Because earlier grab-sample measurements had shown no variability among three locations at 1-meter (3-foot) intervals along a line halfway between two wells (623, 625) and parallel to ground-water flow, ten samplers were buried there at 1-meter (3-foot) intervals along the same line. Results from these samplers were used to evaluate the short-range variability of results along the direction of contaminant flow.

In a study to evaluate the short-range variability of results perpendicular to the ground-water flow direction, additional samplers were placed 9.6 meters (30 feet) and 12.8 meters (40 feet) to the east (towards higher concentrations) of well 631. Statistical evaluation of these results will help indicate the spatial resolution, the minimum distance between samplers to obtain statically significantly different resuls of the technique at this site.

Sampler Efficiency

To determine whether the samplers trapped all of the VOCs that diffuse upward into the manifold from the soil or actually sample the VOC concentration, an additional study was carried out. At all 6 wells, manifolds containing two organic vapor monitors were deployed 1 meter (3 feet) to the south of the sampler 6.4 meters (20 feet) to the east of each well. The sums of the amounts of chloroform collected by the two monitors in one manifold were compared with the amount collected by a single-monitor manifold nearby.

Evaluation of the Performance of LPSS the Above Benzene/Chlorobenzene Plume

Four samplers were placed in a 1-meter square (3-foot) pattern at 0.3 meters (1 foot) depth at a location 6.4 meters (20 feet) south (upgradient) of the well with the highest concentrations of benzene and chlorobenzene. Because neither compound was detected in soil gases in the earlier study, these samplers were left in place for three months. This extreme exposure time was provided so that detection of very low concentrations of either compound would be assured.

RESULTS AND DISCUSSION

PERFORMANCE OF THE LPSS ABOVE THE CHLOROFORM GROUND-WATER PLUME

Correlation With Ground-Water Data

Results of chloroform analyses of all of the organic vapor monitors from samplers around wells are listed in Table 4. Table 5 lists the ground-water chloroform concentrations from each well. The mean results from the four symmetrically placed sampling locations surrounding each well, and the soil-gas concentration from samples around that well as measured by a grab-sample and on-site analysis technique in an earlier study. The two soil-gas data sets correlate very strongly ($r^2 = 0.95$) The soil-gas measurements from this study correlate above the 95 percent confidence level with the ground-water data. This indicates that soil-gas measurement by the method used in this study can provide a good picture of VOC contamination in underlying ground water.

Correlation With Grab-Sampling Data

Table 6 lists the sampling locations from this study, the results obtained, and the chloroform concentrations at a 1.3-meter (4-foot) depth at corresponding locations in an earlier EMSL-Las Vegas study (1). Linear regression of these two data sets indicates that there is a correlation of greater than 99 percent significance between them. Figure 6 is a scatter plot of the results from this study as a function of the results from soil-gas measurements made at a depth of 1.3 meters (4 feet) in an earlier study, using the data in Table 6. It can be seen that an excellent correlation exists.

Figure 7 shows the soil-gas data from this study, and the soil-gas and ground-water chloroform concentrations from an earlier study (1) plotted as a function of distance across the plume. It can be seen that the soil-gas measurements clearly agree with the location of the plume as indicated by ground-water analyses.

Short-Range Variability

In an effort to assess the overall precision (analytical, sampling, and geologic variability) of the technique, the variance of the results from the groups of closely spaced samplers 6.4 meters (20 feet) south of the six wells was calculated. Table 7 lists the individual results and the mean and standard deviation of each group with detectable concentrations.

The standard deviations comprise a linear function of the measured concentration. A composite function of the standard deviation of the soil-gas data as a function of concentration and the concentration as a function of distance has been obtained (33). Using this relationship, the minimum distance across the plume from each sampling location where a statistically significantly different concentration would be observed can be calculated (33). Table 8 lists the distance east of well 631 and the observed concentration for the southern sampling locations in this study. In addition, the table lists the distances east and west from the sampling locations where linear interpolation predicts that a statistically significantly different concentration will be measured. This distance has been called the spatial resolution of soil-gas measurement (33). It is of interest that the values at wells 623 and 629 are quite different although the observed concentrations are the same (2.6 ppbv). This could be due to differences in geologic features beneath the two locations.

TABLE 4. RESULTS OF ANALYSES OF ORGANIC VAPOR MONITORS FOR CHLOROFORM

Well	Sampler	Mass Collected (ng)[a]	Corrected Mass Collected[b]	ppb
621	N	0.21	0.03	NDb
	S1	0.11	----	ND
	S2	0.15	----	ND
	S3	0.14	----	ND
	S4	0.15	----	ND
	E1	0.15	----	ND
	E2a	0.10	----	ND
	E2b	0.08	----	ND
	W	0.20	0.02	ND
623	N	9.73	9.58	2.7
	S1	12.51	12.33	3.4
	S2	8.46	8.28	2.3
	S3	10.44	10.26	2.8
	S4	7.28	7.10	1.9
	E1	6.05	5.87	1.6
	E2a	3.93	3.75	1.0
	E2b	2.38	2.23	0.6
	W	21.14	20.96	5.7
624	1	56.92	56.75	15.5
	2	52.98	52.81	14.4
	3	44.56	44.38	12.1
	4	64.93	63.76	17.4
	5	51.19	51.01	13.9
	6	53.72	63.54	14.6
	7	45.54	45.36	12.4
	8	47.84	47.66	13.0
	9	60.31	60.13	16.4
	10	48.90	48.72	13.3
625	N	72.45	72.27	20.3
	S1	68.20	68.02	18.6
	S2	43.96	43.78	12.0
	S3	55.48	55.30	15.1
	S4	52.31	52.13	14.2
	E1	86.18	86.00	23.5
	E2a	70.17	69.99	19.1
	E2b	75.63	75.45	20.6
	W	43.24	43.06	18.1
627	N	32.12	31.94	9.0
	S1	28.13	27.95	7.6
	S2	26.42	26.24	7.2
	S3	23.81	23.63	6.5
	S4	19.96	19.78	5.4
	E1	42.09	41.91	11.4
	E2a	35.51	35.33	9.6
	E2b	35.37	35.19	9.6
	W	15.11	14.93	4.1
629	N	10.57	10.39	2.9
	S1	11.00	10.83	3.0
	S2	9.31	9.13	2.5
	S3	8.30	8.12	2.2
	S4	10.79	10.61	2.9
	E1	5.54	5.36	1.5
	E2a	4.41	4.23	1.2
	E2b	4.03	3.85	1.0
	W	4.27	4.09	1.2
631	N	0.20	0.02	ND
	S1	0.105	----	ND
	S2	0.111	----	ND
	E30	0.14	----	ND
	E40	0.26	0.08	2 x 10-2
	E1	0.10	----	ND
	E2a	0.06	----	ND
	E2b	0.06	----	ND
	W	0.12	----	ND

[a]
[b] Correction for blank = 0.18 ng.
Detection limit = 0.02 ppb (3 x standard deviation of blanks)

TABLE 5. COMPARISON OF SOIL-GAS PASSIVE AND GRAB SAMPLING RESULTS WITH GROUND-WATER ANALYSES

Well	Ground-Water Chloroform Concentration (μg/L)	*Mean Soil-Gas Chloroform Concentrations (ppbv)*[a] Passive Sampling at 0.3 Meters (1 ft)	Grab Sampling at 1.3 meters (4 ft)
621	28	ND	11
623	555	3.2	40
625	866	19.2	370
627	175	7.8	68
629	11	2.0	23
631	ND	ND	5

[a] Means of all points sampled at each well.

TABLE 6. COMPARISON OF RESULTS FROM PASSIVE AND GRAB SAMPLING METHODS

Well	Sampling Location	*Mean Soil-Gas Chloroform Concentrations (ppbv)* Passive Sampling at 0.3 Meters (1 ft)	Grab Sampling at 1.3 meters (4 ft)
621	N	ND[a]	b
	E	ND[a]	b
	S	ND[a]	b
	W	ND[a]	11.0
623	N	2.7	12
	E	1.6	6
	S	2.6[c]	27
	W	5.7	115
624[d]		14.3[f]	150[e]
625	N	20.3	326
	E	23.5	376
	S	15.0[c]	511
	W	18.1	266
627	N	9.0	73
	E	11.4	125
	S	6.7[c]	46
	W	4.1	28
629	N	2.9	25
	E	1.5	27
	S	2.6[c]	31
	W	1.2	10
631	N	ND[a]	b
	E	ND[a]	5
	S	ND[a]	b
	W	ND[a]	b

[a] ND = Not detected after subtraction of blank results.
[b] Not sampled.
[c] Mean of four samples in a 1-meter square pattern (see text).
[d] Location 624 halfway between wells 623 and 625.
[e] Mean of three points separated by 1 meter each along a north-south line.
[f] Mean of ten points separated by 1 meter each along a north-south line.

FIGURE 6. SCATTER PLOT OF PASSIVE-SAMPLING VERSUS GRAB-SAMPLING RESULTS

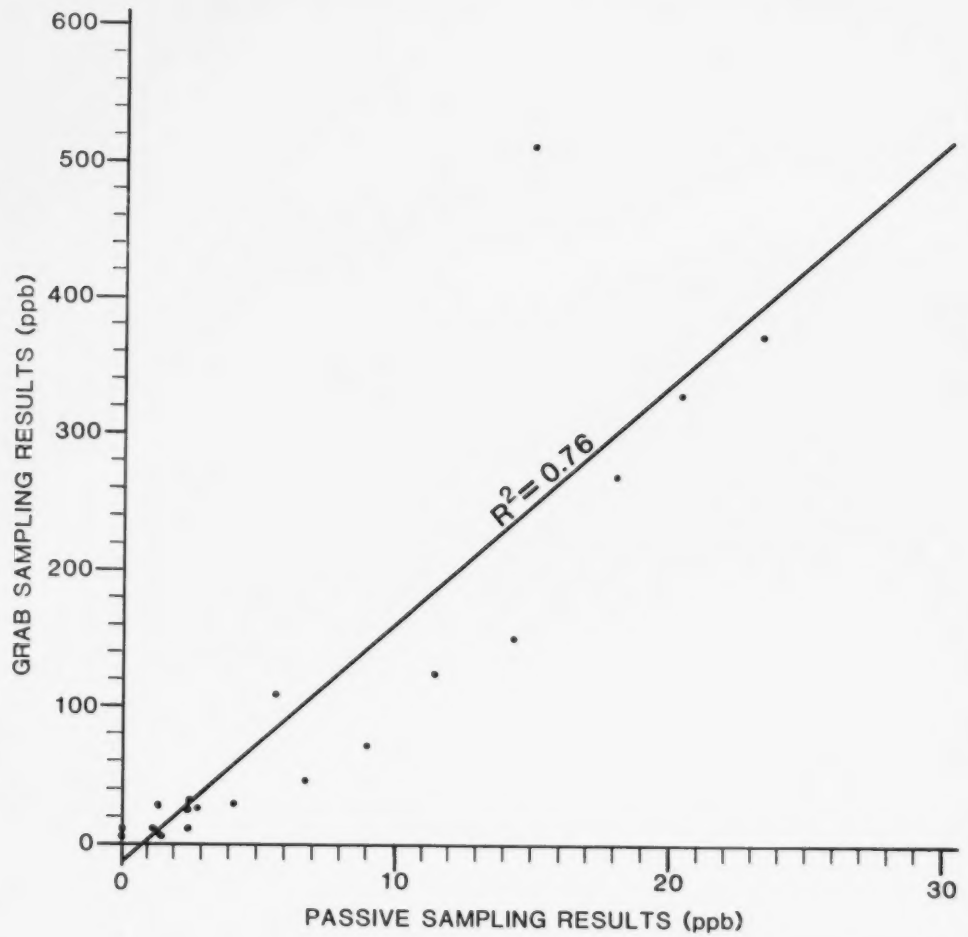
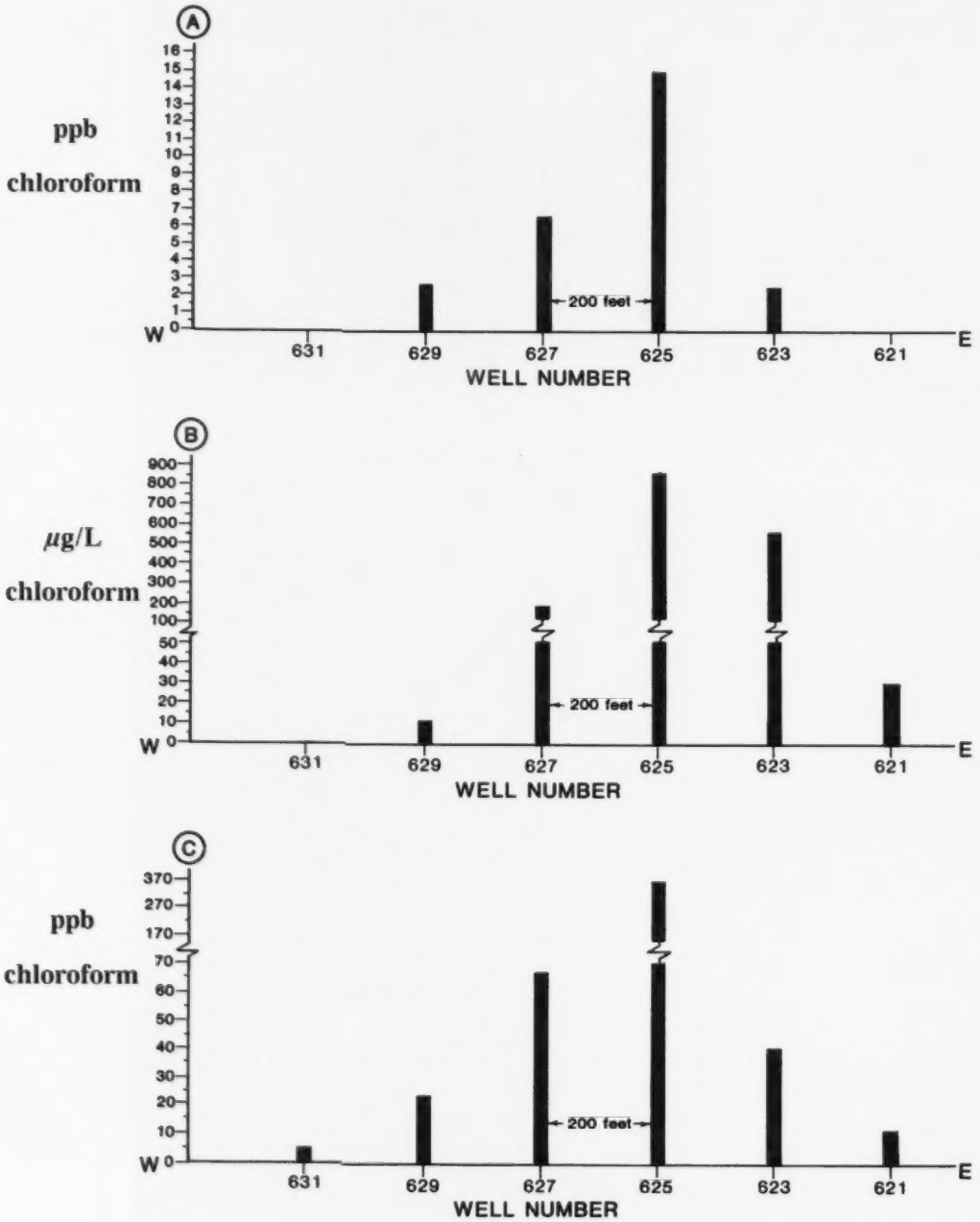


FIGURE 7. GRAB-SAMPLE AND LPSS PASSIVE-SAMPLING SOIL-GAS CHLOROFORM CONCENTRATIONS AND GROUND-WATER CHLOROFORM CONCENTRATIONS



A: Passive sampling soil-gas chloroform concentrations
B: Ground-water chloroform concentrations
C: Grab sampling soil-gas chloroform concentrations

TABLE 7. RESULTS OF CLOSELY SPACED PASSIVE SOIL-GAS SAMPLERS

Well	Sampler	Chloroform Concentration (ppbv)	Mean Chloroform Concentration (ppbv)	Standard Deviation
623	S-1	3.37		
	S-2	2.26		
	S-3	2.80	2.6	0.6
	S-4	1.94		
625	S-1	18.6		
	S-2	12.0		
	S-3	15.1	15.0	2.7
	S-4	14.2		
627	S-1	7.6		
	S-2	7.2		
	S-3	6.5	6.7	1.0
	S-4	5.4		
629	S-1	3.0		
	S-2	2.5		
	S-3	2.2	2.6	0.4
	S-4	2.9		
624[a]	1	15.5		
	2	14.4		
	3	12.1		
	4	17.4		
	5	13.9	14.3	1.7
	6	14.6		
	7	12.4		
	8	13.0		
	9	16.4		
	10	13.3		

[a] Location 624 is a north-south line halfway between wells 623 and 615.

TABLE 8. SPATIAL RESOLUTION OF SOIL-GAS MEASUREMENTS BY PASSIVE SAMPLING

Well	Mean Chloroform Concentration (Standard Deviation)	Spatial Resolution (Feet)
631	ND[a]	--
629	2.6 (0.4)	43
627	6.7 (1.0)	53
625	15.0 (2.7)	67
623	2.6 (0.6)	9
621	ND[a]	--

[a] ND = Not detected after subtraction of blank results.

Sampler Efficiency

The efficiency of the sampler/manifold assembly was assessed by comparison of the results of analysis of two monitors in the same manifold to the results of analysis of a single monitor in a manifold located 1 meter (3 feet) away. The hypothesis for this comparison was that if the sum of the amount collected by two monitors is close to twice the amount collected by a single monitor in a manifold the technique measures concentration and the sampling rate is not limited by the rate of diffusion of chloroform from the soil into the manifold. On the other hand, if the sum of the amount of chloroform collected by the two monitors in a can is essentially equal to the amount collected by the single-monitor assembly, the sampling rate is determined by the rate of diffusion of chloroform into the manifold.

The "efficiency" value listed in Table 9 is the amount of chloroform collected by the single-monitor sampler divided by the sum of the amounts collected by each vapor monitor in the dual-monitor sampler. When the accumulation rate is limited by the rate of supply of chloroform from the vadose zone into the sampler, that value will approach unity. When the rate of accumulation of chloroform was determined by the concentration in the manifold, that value will approach 0.50.

TABLE 9. SAMPLER EFFICIENCY STUDY RESULTS

Well	Sampler	Chloroform Concentrations	Efficiency
623	E-1	1.60	0.98
	E-2a	1.02	
	E-2b	0.61	
625	E-1	23.5	0.59
	E-2a	19.1	
	E-2b	20.6	
627	E-1	11.4	0.59
	E-2a	9.6	
	E-2b	9.6	
629	E-1	1.5	0.68
	E-2a	1.2	
	E-2b	1.0	

It can be noted that the efficiency listed in Table 9 decreases with decreasing concentration. This calls into question the applicability of **Equation 2** in this situation. For **Equation 2** to be applicable the sampling rate of the monitor must not affect C_a, the gas-phase concentration being sampled. This requires a supply of VOC more rapid than the monitor sampling rate. In the workplace atmosphere, where these monitors are used routinely, this supply rate is ensured by air currents. In soil gases, where bulk air movement is very slow, this rate of supply is equal to the vertical VOC flux. In this study, the vertical flux of chloroform is expected to be directly proportional to the groundwater chloroform concentration according to current theory (4,9) so that the low groundwater chloroform concentrations are expected to produce commensurately lower vertical fluxes of chloroform. However, this would not affect the applicability of **Equation 2** (*vide supra*), because the sampling rate of the monitor is directly proportional to the gas-phase concentration. Since the chloroform concentration at the sampling

locations is proportional to the groundwater concentration, as is the vertical flux, the ratio of the chloroform mass accumulation rate to the vertical flux of chloroform should be fairly constant given consistent subsurface characteristics (11).

Because the soil-gas moisture content is expected to be relatively constant among the sampling locations (34) humidity effects could only have caused our observations if the effects of humidity on charcoal sorption efficiency increase with decreasing chloroform concentration. Such a situation has been observed for activated carbon sorption of another chlorinated compound, trichloroethene (35). The data in that study fit the Dubinin-Polyani equation for sorption.

PERFORMANCE OF THE LPSS ABOVE BENZENE/CHLOROBENZENE GROUND-WATER PLUME

Analysis of all four LPSS samplers from above the benzene/chlorobenzene ground-water plume did not show detectable amounts of either compound. The minimum detectable amount of each compound on the monitor is 10 milligrams; on the basis of the monitor sampling rate and a 3-month exposure time, concentrations of one part per trillion by volume of benzene or chlorobenzene would be measureable.

This result confirms the results obtained with the grab-sample study performed earlier at this site (1). In that study, many compounds were observed in soil gases above the benzene/chlorobenzene ground-water plume but benzene and chlorobenzene were not. The absence of these compounds in the soil-gas was attributed to extensive aerobic biodegradation in the shallow vadose zone at the site. In that study, none of the other compounds present in the soil gases were identified. Small amounts (below 10 milligrams) of diethyl ether,isopropyl ether, ethylene dibromide (EDB), and ethyl acrylate were observed. The identities of the compounds are consistent with intermediates in aerobic biodegradation of hydrocarbons (ethers and esters). Several other (unidentified) compounds were also detected.

QUALITY CONTROL

Field and laboratory blank monitors showed no contamination. However, the desorption solvent (hexane) used for chloroform contained chloroform equivalent to approximately 0.018 ppbv; this was subtracted from all results. The detection limit was 0.02 ppbv for chloroform and approximately 1 part per trillion by volume for benzene and chlorobenzene. Monitors sealed in manifolds for four weeks showed no detectable benzene, chlorobenzene, or chloroform.

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